

REMARKS/ARGUMENTS

The claim 1 has been amended to recite a preferred range for the relative humidity of the regeneration gas, (i.e. from 5 to 60%), a preferred temperature range (i.e., 200 to 400°C), and a preferred pressure range (i.e., 30 to 120 bara). The beneficial results obtained through the use of this combination of relative humidity, temperature and pressure is also now recited in claim 1. Claim 1 has additionally been amended to specify the percent water that is removed by the first zeolite. Support for these amendments is found on page 11 of the specification, lines 24-32 and page 6, lines 29-31.

Claims 5 and 14 have been amended to specify the hydrocarbon stream is a gaseous stream. Support for this amendment can be found on page 4, lines 5-10.

The amendments to claims 7 and 20 are similar to those made to claim 1, and are supported by the same disclosures referred to in connection with claim 1.

Claims 8, 12, 14 and 25 have all been amended to include the preferred relative humidity range between 10 and 30% for the regeneration gas. Support for this amendment is found on page 11 of the specification, lines 24-26.

Claims 10 and 23 have been amended to include preferred temperature and pressure ranges for the regeneration step, which ranges are disclosed on page 11 of the specification, lines 26-32.

The claims as amended are believed to be clearly distinguishable over the prior art of record as discussed below.

The Present Invention

The present invention is based in part on the discovery that the degradation/ageing of sulfur loaded zeolite adsorbents used to remove sulfur from gaseous hydrocarbon streams can be significantly reduced by regenerating the adsorbents using a regeneration gas having a specified small amount of water present in the regenerating gas (specification, page 3, lines 25-32). The presence of small amount of water in the regenerating gas, i.e., “wet” regeneration, has been found to extend the capacity of the adsorbent through repeated adsorption/regeneration cycles. This is shown in Table 1 on page 13 of the present application, where the capacity of the adsorbent after 50 cycles of conventional “dry” regeneration was reduced from 19.2 to 12.1 (a

37% decrease) while the capacity of the adsorbent after 50 cycles of “wet” regeneration in accordance with the invention was reduced from 17.4 to 16.7 (only a 4 % decrease). This is rather surprising in that presence of water under certain conditions has been known to cause hydrothermal ageing of zeolite adsorbents, reducing the economic life of a zeolite adsorbent, rather than extending it as is the case with the present process.

Each of the amended claims, either directly or through dependency, contains a limitation requiring that the regeneration gas used to regenerate the sulfur loaded adsorbent contain a certain amount of water expressed in terms of relative humidity, i.e., either between 5 and 60% or between 10 and 30% relative humidity. In addition, the amended claims now specifically recite the benefit of reduced degradation and ageing of the adsorbent obtained by practice of the present process. The “wet” regeneration of a sulfur loaded adsorbent with a regenerating gas containing the specified relative humidities, and the benefits thereby obtained, are not taught or suggested by any of the references previously cited against the application as discussed below.

In addition to the regeneration of the sulfur loaded adsorbent with a regeneration gas having a specified relative humidity, another important feature of the present invention is the removal of water from the hydrocarbon feed stream with an adsorbent comprising a first zeolite having a pore diameter of less than 5Å, prior to contacting the hydrocarbon stream with a second zeolite adsorbent having a pore diameter of at least 5Å to adsorb the sulfur compounds, which sulfur loaded second zeolite adsorbent is regenerated using a regeneration gas having a specified relative humidity as described above. This particular combination of steps, including “wet” regeneration, is also not taught or suggested by any of the previously cited references as discussed below.

GB 2,275,625 (GB’625)

Turning now to the prior art, GB ‘625 patent teaches a process for removing hydrogen sulfide and organic sulfur from a gas stream by first passing it to an absorber system wherein it is contacted with an aqueous absorbent to remove hydrogen sulfide and mercaptans therefrom. The thus-treated gas having a decreased content of hydrogen sulfide and mercaptans is then passed to an adsorbent system such as first adsorber 22, in Fig. 1/1, wherein it is contacted with a solid adsorbent such as a molecular sieve to remove additional mercaptans and water therefrom to provide a purified gas stream. The solid adsorbent is thereafter regenerated in a second adsorber

23 using a bleed stream of the purified gas which flows through heater 44 and conduit 31b. Since any water present in the feed gas to first adsorber 22 will be removed by the by the adsorbent in first adsorber 22, the regeneration of the adsorbent in second adsorber 23 with a bleed stream of purified gas in the second adsorber 23 is a conventional “dry” regeneration. There is no teaching or suggestion in GB ‘625 of “wet” regeneration of a sulfur loaded adsorbent, which involves the use of a regeneration gas stream having a specified amount of added water to regenerate the loaded adsorbent.

In fact, GB ‘625 actually teaches using the regeneration gas to remove water adsorbed on the adsorbent. See the disclosure on page 4, lines 12-18 of GB ‘625, wherein it is stated that:

“The solid adsorbent can in addition to removing mercaptans remove water from the treated gas. With the regeneration off-gas water is removed from the solid adsorbent, and to remove water from the regeneration off-gas, the regeneration off-gas is cooled in a cooler (not shown) and liquid water is separated in a gas-liquid separator (not shown) which cooler and separator are arranged in conduit 47 ”.

There is absolutely no indication that the bleed stream of purified gas used for regeneration in GB ‘625 contains a relative water humidity, nor is there any teaching or suggestion in GB ‘625 that using a regeneration gas containing the specified relative humidity will significantly reduce degradation/ageing of a zeolite adsorbent, as discovered by Applicant and recited in the amended claims.

Gingrich et al

Gingrich et al teaches a process for removing contaminants from a gas stream to unprecedentedly low levels by the use of four sequential beds of solid adsorbents. The first bed of adsorbent is used to remove water, while the following beds are used to remove various types of sulfur compounds and other contaminants such as fluorocarbons and halocarbons. Gingrich et al does not contain any teaching or suggestion relating to regeneration of any of the adsorbents used in any of the four sequential beds. The concept of a regeneration gas stream having a specified relative humidity is totally lacking in Gingrich et al, which apparently is only being cited for its teaching of a first adsorbent bed to remove water prior to a second and third adsorbent bed to remove sulfur-containing compounds.

Thus, it can be seen that neither GB '625 nor Gingrich et al teach or suggest regenerating a sulfur loaded adsorbent by contacting the loaded adsorbent with a regeneration gas stream having a specified relative humidity. Since all of the amended claims, either directly or through dependency, contain a limitation as to the relative humidity of the regenerating gas stream, which results in the significantly reduced degradation/ageing of the adsorbent, all of these claims are believed to be patentable over these references, alone or in combination.

Sherman et al

Sherman et al teaches a process for purifying hydrocarbon gas streams containing H₂S and CO₂ as impurities using molecular sieve adsorbents, wherein the principle object of the invention is to provide a means to suppress the formation of COS (Col. 1, lines 59-63). The basic process disclosed in Sherman et al includes the steps of (a) an adsorption purification stroke wherein H₂S is selectively removed and a substantially H₂S-free hydrocarbon product is recovered; (b) a purge desorption stroke wherein a portion of the hydrocarbon product is heated and passed countercurrently through the adsorption bed to desorb substantially all of the adsorbate molecules selectively adsorbed in step (a); and (c) a cool down stroke wherein the bed is cooled down by cocurrent purge using a portion of the H₂S-free hydrocarbon product. The improvement claimed in Sherman et al is the use of a particular zeolite having a pore diameter of at least 5 Å and at least 45 % of the framework of aluminum atoms being associated with at least one species of an alkaline earth metal cation having an atomic number of less than 56, and injecting into the hydrocarbon stream prior to step (b) a sufficient amount of water vapor to import a substantially uniform adsorbed water loading of from 0.7 to 3.0 wt % to the molecular sieve adsorbent (Col. 2, lines 14-25).

There is no teaching or suggestion in Sherman et al of removing water from hydrocarbon gas stream using a zeolite having a pore diameter less than 5 Å prior to contacting it with the molecular sieve having a pore diameter of at least 5 Å to remove sulfur compounds.

While Sherman et al does teach the injection of water vapor into the hydrocarbon stream prior to purge step (b), the purpose of the addition of water vapor is to import a substantially uniform adsorbed water loading of 0.7 to 3.0 wt % to the molecular sieve adsorbent, which percentage of water has been found to suppress COS formation. There is no teaching or suggestion in Sherman et al that using a regeneration gas having the amounts of relative water

humidity specified in the present claims will substantially reduce the degradation/ageing of the adsorbent as discovered by Applicant and recited in the amended claims.

Turnock et al

Turnock et al discloses a process for removing sulfur compounds from liquid hydrocarbon streams, such as natural gasoline, using a zeolitic molecular sieve dehydrated only to the extent that it contains a residual loading of water of from about 2 to about 5 weight percent (col.1, lines 4-10).

It is stated in column 2, lines 4-14 of Turnock et al that:

“In accordance with the present invention it has been surprisingly found that the presence of relatively large amounts of residual adsorbed water on large pore zeolitic molecular sieve adsorbents does not diminish their capacity for adsorbing sulfur-containing impurities from liquid hydrocarbon streams. In marked contrast to this finding, it is well known that in vapor phase-sweetening processes, the presence of even relatively small amounts of water on the molecular sieve adsorbent has such an adverse effect on its selectivity and capacity as to render the operation commercially unfeasible”.

According to Turnock et al the above-described discovery makes it possible to carry out the thermal-swing desorption of the sulfur-containing compounds from the molecular sieve adsorbent using a purge gas having a high water content. It is even possible, and in fact preferred, to use steam as the purge gas (col. 2, lines 29-36). The water contents needed in the regeneration gas at various temperatures and pressures to leave from about 2 wt. % to about 5 wt. % H₂O on the adsorbent are given in col. 6, lines 5-31.

Thus, in its most relevant aspects, Turnock et al discloses a thermal-swing desorption step using a purge gas having a high water content, preferably steam, to regenerate the molecular sieve adsorbent to a residual water loading of a 2-5 wt %. There is no teaching or suggestion in Turnock et al of using a regeneration gas having a specified relative humidity for the purpose of substantially reducing the degradation/ageing of the adsorbent over repeated cycles.

In addition, there is absolutely no teaching or suggestion in Turnock et al of removing water from hydrocarbon gas stream using a zeolite having a pore diameter less than 5Å prior to contacting it with the molecular sieve having a pore diameter of at least 5Å to remove sulfur compounds. While Gingrich et al does disclose the use of a first adsorbent bed to remove water,

Gingrich et al cannot logically be combined with Turnock et al, because the process in Gingrich et al involves removing sulfur-containing compounds from gases, i.e., it is a vapor-phase sweetening process. Turnock et al expressly states that: “it is well known that in vapor phase-sweetening processes, the presence of even relatively small amounts of water on the molecular sieve adsorbent has such an adverse effect on its selectivity and capacity as to render the operation commercially unfeasible” (col. 2, lines 10-14). (Underlining added for emphasis). Hence, one skilled in the art would not combine the liquid phase sulfur removal process of Turnock et al (which employs adsorbents having relatively high water loadings) with the gas phase sulfur removal process of Gingrich et al, because such combination according to Turnock et al would render the process unfeasible.

It is noted that Turnock et al discloses the pressure conditions employed in the adsorbent bed during regeneration range from 15 -100 p.s.i.a. and goes on give a range of dew point levels at various temperatures for this pressure range (col. 5, line 75 to col. 6, line 25). The pressure range of 15-100 p.s.i.a. disclosed in Turnock et al equals approx. 1.0 to 6.9 bara, which is well below the regeneration pressure of between 30 and 120 bara, or between 50 and 90 bara, specified in the present claims. Thus the present claims are distinguishable from Turnock et al for this reason as well.

It is further noted that amended claims 5 and 14 specify the hydrocarbon stream from which the sulfur compounds are removed is a gaseous hydrocarbon stream. Thus, these claims are believed distinguishable over Turnock et al for this reason, in addition to those discussed above.

For all of the above reasons, it is believed that the present claims, as amended, are patentable over the references of record. Accordingly, it is respectfully requested that the claims be allowed and the application passed to issue.

Respectfully submitted,

JOLINDE MACHTELD VAN DE GRAAF and
THIJME LAST

By Charles W. Stewart/

Their Attorneys, Charles W. Stewart
and Leonard P. Miller
Registration Nos. 34,023 and 26,004
(713) 241-0360

P. O. Box 2463
Houston, Texas 77252-2463